

A Chromophoric Dissolved Organic Matter (CDOM) Observatory

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LONG-TERM GOALS

The long-term goal of this project is to develop an understanding of coastal systems such that optical properties of complex coastal waters can be retrieved and predicted from remote sensing and modeling efforts.

OBJECTIVES

This project focuses on establishing a moderate-scale observatory (Neponset) to develop watershed and coastal ocean models and remote sensing algorithms and extending this knowledge to a larger system (Hudson).

Specific Objectives:

- 1) Design and deploy CDOM observatory components in the Neponset Estuary and Boston Harbor.

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- 2) Refine remote sensing algorithms for CDOM in the Neponset Estuary, Boston Harbor, and Massachusetts Bay based on high resolution and/or hyperspectral satellite imagery ground-truthed within the CDOM Observatory.
- 3) Refine a predictive watershed model for CDOM sources based on a Soil Water Assessment Tool (SWAT) and Geographical Information Systems to predict sources of CDOM to the estuary.
- 4) Refine the existing Boston Harbor physical/biogeochemical model to provide a 3-day forecast of CDOM distributions in Boston Harbor.
- 5) Observe CDOM distributions and processes in the Neponset Watershed and Estuary and Boston Harbor for at least 12 months and refine observation protocols and predictive modeling capabilities.
- 6) Develop “smart” network to respond to episodic events.
- 7) Extend and deploy CDOM observatory in the Hudson Estuary for a 2-week period to show general applicability of the observation and prediction capabilities. This has been done while using the CDOM distribution model developed by Alan Blumberg at the Stevens Institute of Technology.

APPROACH

The CDOM Observatory is composed of five major components: continuous monitoring stations, targeted sampling, remote sensing, watershed and coastal modeling, and cyberinfrastructure. Initial focus for all monitoring, sampling, and remote sensing activities was in the Neponset Watershed, Neponset Estuary, and Boston Harbor. In August, 2010 (Year 2), the CDOM Observatory will be redeployed in the Hudson Watershed and Estuary to determine the transferability of the Observatory.

Bernie Gardner and Francesco Peri were responsible for development, deployment, and maintenance of the CDOM observatory—the continuous monitoring stations in the estuary and watershed, and integration of the autonomous underwater vehicle (AUV). Watershed modeling and remote sensing was carried out by Yong Tian who has developed remote sensing algorithms for CDOM based on hyperspectral radiometric measurements in the Gulf of Mexico and Hudson Estuary. Estuarine/coastal modeling was carried out by Mingshun Jiang who maintains a Boston Harbor/Massachusetts Bay predictive model.

WORK COMPLETED

Five low-cost (<\$10k) buoys were designed, constructed and deployed in the Neponset Estuary/Boston Harbor area. CDOM, water temperature, and chlorophyll fluorescence, as well as current direction, wind speed and direction, barometric pressure, relative humidity, and PAR are being measured. Real-time data is available at <http://www.cesn.org/livedata.php>. In all, buoys have been operational and gathering Boston Harbor data for 25 ice-free months over the course of this project.

These buoys have been deployed in summer and fall, 2009, but were damaged in the winter due to freezing and thawing affecting the integrity of the housings. We have recovered them, fitted them with salinity sensors, and redeployed them in 2010. After some further power issues, they were redployed in 2011. During deployment, optical sensors were maintained by manually wiping the windows approximately every 2 weeks.

An autonomous underwater vehicle (AUV; YSI EcoMapper) has been purchased, tested and deployed in Boston Harbor. Autosampling units for watershed samples have been purchased, fitted with wireless telemetry, and deployed automatically (triggered by rainfall sensor) over the summer, 2011 in the Neponset Watershed to examine episodic rain events. 31 stations throughout the Neponset Watershed are continuing to be sampled monthly (>40 month record) and analyzed for dissolved organic carbon (DOC) and chromophoric dissolved organic matter (CDOM) in the form of fluorescence and absorption spectra and occasional excitation-emission matrix spectroscopy (EEMS). Over the last 3 years, 13 monthly Mini-Shuttle transects up the Neponset Estuary have been conducted. EO-1 satellite imagery has been procured in 2009. Our hyperspectral (Applied Spectral Devices; ASD) radiometer mounted on the bow of our research vessel has been useful in correlating the surface reflection with *in situ* CDOM measurements. Our Boston Harbor model has been refined to increase the resolution to a 10-meter grid size in the Neponset Estuary portion of the Boston Harbor.

We deployed our small boat with a tow-yo Mini-Shuttle package, ECOShuttle, and shore stations in the Hudson Estuary in August, 2010. The Mini-Shuttle, shore stations and autosamplers have been deployed in Snipe Creek, Florida to study CDOM outwelling from salt marshes. Overall, these deployments have proven that the CDOM observatory is mobile and adaptable, and can be used to study CDOM in a variety of coastal systems at spatial and temporal resolution that was not possible before.

We have made three major refinements to the predictive watershed model for CDOM sources. First, the Soil Water Assessment tool (SWAT) model has been re-calibrated to incorporate soil data in the SURGO database (county-level replaced state-level data, STATSGO). Second, we improved the model responses to agricultural and forest lands by calibrating the model with a new data set collected from non-residential watersheds. Third, the model has been extended to include climate variables (temperature and precipitation). The model works for existing observations and is also able to project future scenarios considering climate change. An extra effort in spring, 2011 was made by measuring snow melt effects on in-stream DOC dynamics to improve model performance during snow melting season.

RESULTS

Our Neponset CDOM Observatory continues to be developed, but so far has yielded valuable results. Our data set of over 40 months of 30 samples distributed throughout the watershed has allowed us to understand the dependence of CDOM endmember values on land use, season and discharge. A simple model can use these parameters to predict the endmembers with an r^2 of 0.4 to 0.7 (Huang and Chen, 2009). This same simple model has been applied to the Hudson Watershed with approximately the same reliability (Huang et al., 2011). A more detailed model may increase this reliability to an r^2 of 0.7 to 0.8 (Wang et al., 2010).

The system of real-time buoys, shore stations, and watershed stations has been developed and deployed. The design of the shore stations has been shown to be robust, and the buoys have worked well in non-winter months. Monthly Mini-Shuttle cruises suggest a strong “fall dump” of CDOM from fringing salt marshes. An increase from September through November, then a decrease to near zero in January has been seen for the mid-estuary input contributed by salt marshes over several years (Figure 1). This seasonality has been incorporated into our high resolution circulation model (10 meters resolution). A distributed source contributed at an ebbing tide yields the model results that best match

our observations, although there are still some components of the model (e.g. changing land-water interface) that are still being developed.

Four autonomous profiling moorings were deployed around the Granite Avenue Bridge (2 upstream and 2 downstream) in July, 2010. The moorings were programmed to run a profile from the bottom to the surface and back to the bottom every 15 minutes at a profiling rate of 2 m/min. Each mooring was equipped with a Turner Designs CDOM fluorometer. This high resolution profiling experiment in conjunction with Carrick Detweiler, MIT, (Detweiler et al., 2010) used our Neponset CDOM Observatory as a testbed for computer sensor network software aimed to maximize observations of high spatial gradient oceanic features.

Satellite-based CDOM assessments were explored for the Neponset Estuary using EO-1 Hyperion satellite images. Current ocean color algorithms are mostly limited to open ocean sea water and have high uncertainty when directly applied to turbid coastal waters. We developed a semi-analytical algorithm QAA-CDOM based on a widely used ocean color algorithm QAA and our earlier extension QAA-E (Zhu et al., 2011a). The algorithm development, calibration and validation relied on our intensive high-resolution underwater measurements (in the Neponset River, the Hudson River, and Atchafalaya River), IOCCG synthetic data, and global NOMAD (NASA Bio-optical Marine Algorithm Dataset) (Zhu and Yu, 2011b). An overarching goal of this research has been to improve the algorithm performance for a wide range of water conditions, especially turbid waters in estuarine and coastal regions.

The inversion and validation in the Neponset River and Boston Harbor were based on transects (underwater Mini-shuttle measurements and above-surface ASD spectral measurements) and a Hyperion image acquired on November 4, 2009. The results show that CDOM's absorption coefficient at 440 nm, $a_g(440)$, is able to be estimated from Hyperion images with good accuracy (Error = -0.48 and RMSE = 0.61). Chlorophyll is correlated to the CDOM-inversion error with $R^2 = 0.42$ (Zhu and Yu, 2011c), so we are now pursuing improvements of QAA-CDOM by using high quality satellite images to correct for the chlorophyll interference.

A higher resolution (10 m) model has been developed for the Neponset Estuary based on the same model framework for Boston Harbor and Massachusetts Bay (Jiang, 2011). The model is driven by meteorological forcing and, along the open boundary, by the harbor model. The model domain includes the salt marshes along the river and hence has the potential capacity to test the large episodic CDOM loadings from these areas during flooding period. The model is being tested with the buoy and monthly cruise measurements. The CDOM degradation and production terms (from incubations) are being incorporated into the 10 m Boston Harbor model to better simulate CDOM distributions in the harbor. The rates are parameterized to temperature and salinity based on the regression relationships derived from the monthly measurements in the Neponset Estuary and several cruise measurements in the Hudson River (Huang and Chen, 2009; Huang et al. 2011a).

Geographical Information Systems improved the estimation of DOC delivery from forest species such evergreen, deciduous, mixed forest, and agricultural land. Results indicate that delivery ratios from apicultural land are much higher than that from forests consistently in all outlets. Responses of DOC yields to temperature are linear. Our empirical analysis indicates that a 0.5 °C warming in annual mean temperature would increase annual mean DOC concentrations by 0.2 mg/l in large rivers. Subsequently, DOC export from small urban watersheds is also a function of temperature with slightly greater predicted increases in concentrations (~0.35 mg/L increase) with 0.5 °C warming.

In summary, we have found:

- 1) The Neponset watershed model for predicting CDOM in river endmembers entering the ocean based on land use, season and discharge, is also applicable to the Hudson watershed. More generally, simple watershed modeling has been shown to be useful in supplying temporally varying riverine inputs into estuarine models of CDOM.
- 2) Algorithm development for high resolution satellite remote sensing images suggests that CDOM can be derived at accuracies of $r^2=0.4-0.8$ in turbid estuaries at 30 m resolution. Further algorithm development will address chlorophyll and suspended matter interferences.
- 3) Fall dump and spring snow melt are periods of increased CDOM export that must be included in predictive models of CDOM in estuaries.
- 4) Watershed modeling can predict quantitative changes in carbon dynamics under various climate change scenarios.
- 5) Episodic events (first flush rain events) do alter freshwater endmembers over short (hours to days) timescales.
- 6) Photochemical degradation dominates shorter time scales (1-2 weeks) while bacterial reworking (coupled degradation and concomitant production) of CDOM dominates over longer time scales (>2 weeks) in the Hudson River Plume, resulting in “marine” CDOM entering into the coastal ocean (Huang et al., 2001b).
- 7) Our overall understanding of CDOM dynamics in complex nearshore coastal areas has increased due to modern developments in sensor networks, ocean observation technology, and models.

IMPACT/APPLICATIONS

Our knowledge regarding CDOM source, transport, and fate in estuaries and coastal waters has been greatly expanded. We now have the ability to predict freshwater endmember CDOM based on land use, season, and discharge information. A simple watershed model has been applied to the Neponset and Hudson Watersheds and seems to give reasonable predictions suggesting this approach might be used more widely in many different watersheds. Physical circulation models (eg. Boston Harbor and Hudson Estuary) can use endmember CDOM values as inputs and produce 3-dimensional CDOM predictions for up to 3 days in advance. Rates determined by incubation allow the degradation of CDOM during mixing to be estimated. These predictive capabilities for CDOM appear to allow better prediction of optical water quality.

In addition, we have continued to develop our CDOM algorithms to allow high resolution (30 meter grid size) satellite imagery to be used to measure CDOM in coastal waters. This capability could have a large impact on studying land-ocean transport of dissolved organic carbon as well as studying contaminant plumes, river plumes, or potentially in-water processes (Yu et al., 2010; Zhu et al., 2010).

Several technological advances have also been made. Inexpensive buoys have been designed, redesigned and deployed. Shore stations have been designed and deployed. A system for measuring hyperspectral water-leaving irradiance has been used on 3 different ships. An autosampler has been

fitted for automatic sampling of rivers during episodic events. All of these technological advances will allow high resolution studies of coastal systems.

Watershed and estuarine models can now be linked to confirm high resolution observations. With our current knowledge of the Neponset system, impacts of varying freshwater inputs from rivers, land use changes, salt marshes, and various climate change scenarios on carbon dynamics and optical properties in estuaries can be estimated.

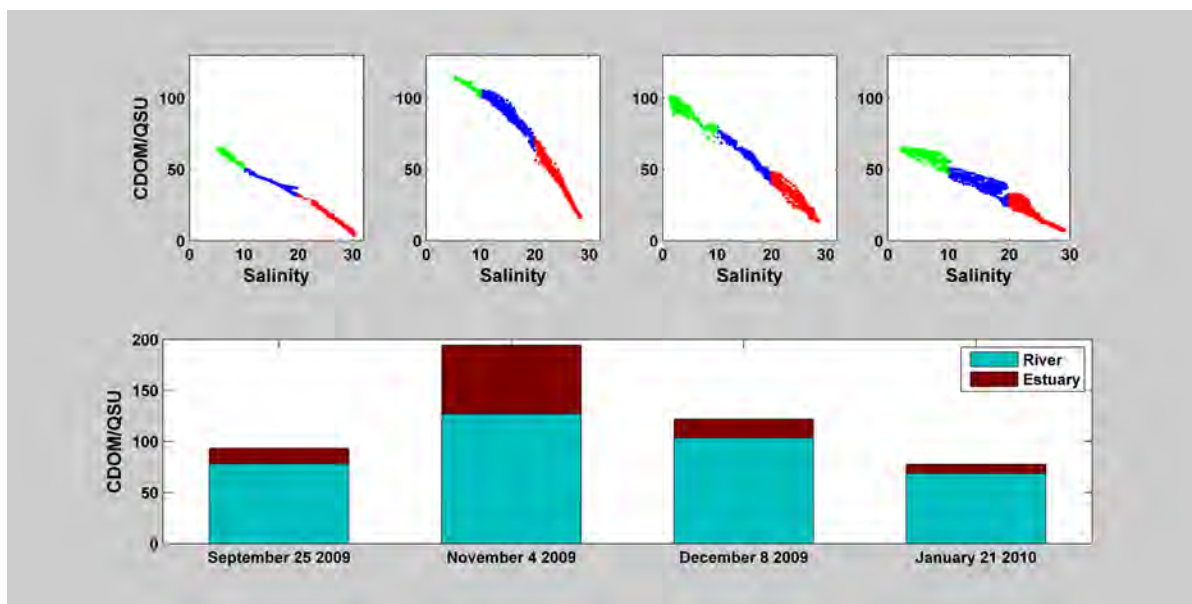


Figure 1: *Plots of chromophoric dissolved organic matter (CDOM) fluorescence vs. salinity in the Neponset Estuary in September, November, December, January (2009-2010). Green data depicts salinities of 0-10; blue, 10-20; and red, 20-30. Note the highest curvature of the data is seen in November as the salt marsh grasses “dump” their carbon into the estuary. The excess CDOM determined from the mid-salinity “apparent” endmember is represented as salt marsh input is shown in the brown in the bottom panel as being highest in November reducing to almost zero in January. River inputs as determined by the extrapolated endmembers of the low salinity data is shown in the blue and also increases in the Fall, but maintains some minimum concentration draining out of the watershed even during the winter.*

RELATED PROJECTS

The Boston Environmental Area Coastal Observation Network (BEACON) project is supported by the Department of Energy. This project within the UMassBoston Center for Coastal Environmental Sensing Networks (CESN) is aimed to provide a testbed sensor network system for testing new sensors, for facilitation collaborations with industry, for learning about the opportunities and barriers to maintaining a nearshore coastal sensor network, and to allow new research opportunities. The BEACON project is integral to allowing the ONR project to focus on CDOM and episodic releases of CDOM.

NASA has supported a project on the “Geospatial Synthesis of Chromophoric Dissolved Organic Matter Distribution in the Gulf of Mexico for Water Clarity Decision Making” (Chris Osburn, PI; Eurico D’Sa, Paula Coble, Tom Bianchi, co-PIs). Data on CDOM export from terrestrial systems into the Gulf of Mexico and related remote sensing data have been useful to this ONR project’s goal to better understand CDOM flow from terrestrial systems to marine systems and to use remote sensing to estimate in situ optical properties.

An NSF-Chemical Oceanography project entitled “DOC Outwelling from Salt Marshes” has been funded. Robert Chen is the PI along with Jennifer Cherrier (FAMU), Jaye Cable (LSU), and Christof Meile (UGA) as co-PIs. This focused study on DOC and CDOM produced in salt marshes helps refine our estuarine models of sources of CDOM to estuaries. Several of the shore station designs for our CDOM observatory have been used in this project, and alternatively, new microdrifter designs generated in the NSF project may be useful in the ONR CDOM observatory in response to episodic events.

MIT SeaGrant has provided support to establish the Consortium for Ocean Sensing In the Nearshore Environment (COSINE), a collaboration between CESN at UMassBoston, Tom Little at Boston University and Ferdi Hellweger at Northeastern University. This 6-year focused area research project examines the use of wireless sensor networks in coastal areas with specific emphasis on coastal inundation, monitoring bacterial water quality, and episodic contaminant release.

PUBLICATIONS

Detweiler, C., Doniec, M., Jiang, M., Schwager, M., Chen, R.F., and Rus, D., 2010. Adaptive Decentralized Control of Underwater Sensor Networks for Modeling Underwater Phenomena. In *Proceedings of 2010 ACM Conference on Embedded Networked Sensor Systems (SenSys 2010)*, Zurich, Switzerland, 2010.

Huang, W. and Chen, R.F., 2009. Sources and transformations of chromophoric dissolved organic matter (CDOM) in the Neponset River Watershed. *J. Geophys. Research-Biogeosciences*, 114, doi:10.1029/2009JG000976.

Huang, W., Chen, R.F., and Gardner, G.B, 2011. Chromophoric Dissolved Organic Matter (CDOM) Cycling in Hudson River Plume. (Submitted to *Estuarine, Coastal and Shelf Science*).

Huang, W., Chen, R.F., and Gardner, G.B, 2012. Chromophoric Dissolved Organic Matter (CDOM) Budgets in Hudson and Tributaries’ Estuaries. In preparation.

Jiang, M., 2011, Intruding flow from Massachusetts Bay and its implications to red-tide blooms in Boston Harbor, to be submitted to *Estuarine, Coastal, and Shelf Sciences*.

Tian, Y.Q., *Wang, D., R. F. Chen and *W. Huang, Using modeled runoff to study DOC dynamics in stream and river flow: a case study of an urban watershed southeast of Boston, Massachusetts, submitted to *Ecological Engineering*.

Yu, Q, 2011, Climate Effects on Dissolved Organic Carbon Export in Seven Major US Coastal Rivers, submitted to *Journal of Geophysical Research-Letters*.

Yu, Q., Y. Q. Tian, R.F. Chen, A. Liu, G.B. Gardner and W.N. Zhu, 2010, Functional linear analysis for estimating riverine CDOM in coastal environment using in situ hyperspectral data, *Photogrammetric Engineering and Remote Sensing*, 76(10), 1147–1158.

Zhu, W.N., Yu, Q., Tian, Y.Q., Chen, R. F., and Gardner, G.B. (2011a). Estimation of chromophoric dissolved organic matter in the Mississippi and Atchafalaya river plume regions using above-surface hyperspectral remote sensing. *Journal of Geophysical Research-Oceans*, 116, C02011

Zhu, W.N., and Yu, Q. (2011b). Inversion of chromophoric dissolved organic matter for turbid estuarine and coastal waters using hyperspectral remote sensing. *IEEE Transactions on Geoscience and Remote Sensing*, in review.

Zhu, W.N., and Yu, Q. (2011c). Uncertainty analysis of remote sensing of colored dissolved organic matter: evaluations and comparisons for three rivers in North America. *ISPRS Journal of Photogrammetry and Remote Sensing*, submitted.